

## **APPENDIX P**

### **FATE AND TRANSPORT CHARACTERISTICS**

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### **FATE AND TRANSPORT PROFILES FOR METALS OF POTENTIAL CONCERN**

As stated in Section 5.0, various metals were detected above screening criteria and/or were identified as chemicals of potential concern (COPCs) and/or chemicals of potential environmental concern (COPECs). A brief discussion of the important controls on fate and transport of these metals of potential concern is presented below. These synopses were compiled from Baes et al. (1984), Clement Associates (1985), and EPA (2014a, 1996a, 1996b, 1986, and 1979), along with other sources (see Section 8.0).

#### **Aluminum (Al)**

In the environment, aluminum exists in only one oxidation state (+3), and does not undergo oxidation-reduction reactions. It can react with other matter in the environment (e.g., other elements such as oxygen, sulfur, or phosphorus) to form various complexes. The fate and transport of aluminum is largely controlled by environmental factors such as pH, salinity, and the presence of various species with which it may form complexes. In general, the solubility and mobility of aluminum in soil is greatest when the soil is rich in organic matter capable of forming aluminum-organic complexes and when the pH is low, such as in areas prone to acid rain or in acidic mine tailings.

#### **Antimony (Sb)**

The hydrogeochemical behavior of antimony is analogous to that of arsenic and, therefore, to iron and manganese as well. Like arsenic, antimony most commonly occurs in the Sb(+3) and Sb(+5) valence states. Antimony in natural waters has not been as well studied as arsenic; however, in existing field and laboratory investigations, antimony also appears to be largely controlled by redox conditions. In aerobic waters, insoluble Sb(V) is adsorbed to ferromanganese oxides and oxyhydroxides; however, the adsorption of Sb(V) may not be as strong as As(V), and the solubility of Sb(V) is generally higher than that of As(V). In anaerobic waters, antimony as Sb(V) is reduced to Sb(III), which is soluble.

The sorptive behavior of antimony is similar to that of arsenic, described in the following section. Antimony is not bioaccumulated in aquatic organisms (BCF of 1 L/kg; EPA, 1986).

#### **Arsenic (As)**

In the environment, arsenic occurs predominantly in the As(+3) and As(+5) valence states and, although certain conditions may promote the formation of arsenious ( $\text{H}_3\text{AsO}_3$ ) or arsenic ( $\text{H}_3\text{AsO}_4$ ) acid, the oxidation state of arsenic is the factor that seems to control arsenic solubilization. The inorganic state is dominant even though arsenic is involved in biological cycling that can form soluble organic complexes. A number of studies have shown that arsenic is both methylated and demethylated during biological cycling, and that the processes seem to more or less cancel each other out.

The redox chemistry of arsenic is highly analogous to that of iron and manganese, and arsenic tends to be closely associated with these two elements in aqueous systems. Under aerobic conditions, As(+5) is the predominant species. Pentavalent arsenic is highly insoluble and tends to be strongly adsorbed on ferromanganous precipitates; i.e., As(+5) follows the oxidized species of iron [Fe(+3)] and manganese [Mn(+4)]. Thus, in oxidized water, arsenic is primarily associated with particulate phases. Under reducing conditions arsenic is reduced to As(+3), which is soluble in anoxic waters. It should be noted that arsenic may also form complexes with anthropogenically introduced organic compounds that may affect the geochemical behavior of arsenic. The arsenate and arsenite ions, when present, may behave in a manner similar to the phosphate ion in aqueous systems (Smith et al., 1995).

Arsenic is adsorbed principally onto clays, aluminum hydroxides, ferromanganese oxides, and organic compounds. In general, pentavalent arsenic has a greater adsorptive affinity than trivalent arsenic. For arsenic, adsorption is most important in aerobic, acidic fresh water with adsorption decreasing above pH 9 for As(+3) and above pH 7 for As(+5). Arsenic is not appreciably bioaccumulated in aquatic organisms (BCF of 44 L/kg; EPA, 1986).

### **Barium (Ba)**

Barium is an alkaline earth element, which is to say that it belongs to Group IIA of the Periodic Table of the elements. Barium is also a geochemical minor element, occurring in most geologic materials in concentrations of a few tenths of a percent to a few percent. Like alkaline earths, barium occurs exclusively in the +2 valence state in nature. The aqueous solubility of barium is low in natural waters. Because of its low solubility, little data are available on the sorption behavior of barium; however, barium is thought to be readily sorbed to clay mineral surfaces. Barium is moderately bioaccumulated in aquatic organisms (BCF of 663 L/kg; ATSDR, 2014).

### **Cadmium (Cd)**

Cadmium may exist in soluble organic complexes or as an ionic species in water. Cadmium ions in solution are always present in the +2 valence state in aqueous environmental matrices and, based upon the site-specific Eh-pH conditions, they are expected to be the predominant species in on-site aqueous matrices. Cadmium may also be associated with the particulate phase. Cadmium is principally adsorbed by clays, organics, carbonates, and aluminum and iron oxides, with adsorption generally increasing as the pH increases. Cadmium is not appreciably bioaccumulated in aquatic organisms (BCF of 81 L/kg; EPA, 1986).

### **Chromium (Cr)**

Chromium is an essential micronutrient that, at elevated levels, can have toxic effects. In aqueous systems chromium can theoretically occur in two oxidation states: Cr(+3) and Cr(+6). In many ways, the hydrogeochemical behavior of chromium is the opposite of iron, manganese, arsenic, and antimony. The oxidized state of chromium, Cr(+6), is relatively soluble, forming complex anions in

aqueous solution. The most important of these are chromate ( $\text{CrO}_4^{2-}$ ) and hydrochromate ( $\text{HCrO}_4^-$ ). However, Cr(+6) species are not stable aqueous complexes under virtually all naturally occurring redox conditions. Hexavalent chromium is stable at Eh approaching and above the limit of atmospheric oxidation. In virtually all natural waters, trivalent chromium [Cr(+3)] is the stable and predominant aqueous form of chromium. In its trivalent form, chromium rapidly precipitates as insoluble oxides or hydroxides, or adsorbs onto clays or oxides of other metals. Chromium is not appreciably bioconcentrated in aquatic organisms (BCF of 81 L/kg; EPA, 1986).

### **Cobalt (Co)**

Cobalt is an essential nutrient that rarely occurs in soluble form in natural aquatic systems, and its hydrogeochemical behavior is therefore little studied. Available evidence suggests that cobalt behavior is analogous to that of iron and manganese in that cobalt is strongly adsorbed to metal oxides and oxyhydroxides, and to clay mineral surfaces. Desorption of cobalt may be important at lower pH values.

### **Copper (Cu)**

Copper is an essential nutrient that, at elevated levels, can have toxic effects. Copper(+2) is the most prevalent form of copper in aqueous systems as most of the stable cuprous (+1) forms in toxic waters are highly insoluble. Copper may also exist in water as the hydrated divalent cupric ion. However, in general, most copper in aqueous solution is in a complex form with organic or inorganic ligands, and these are expected to be the predominant dissolved aqueous species of copper. Copper is sorbed by clays, mineral surfaces, organics, carbonate, and iron and manganese oxide precipitates. Copper adsorption is highly pH dependent, and the presence of other anionic species can increase copper adsorption. Copper is not appreciably bioconcentrated in aquatic organisms (BCF of 200 L/kg; EPA, 1986), since its toxicity to aquatic vegetation and fish limits the extent to which bioaccumulation can occur.

### **Iron (Fe)**

While iron is not typically a constituent of concern, the fate and transport of iron can strongly influence other metals and inorganics due to co-precipitation. The oxidation state of iron is an important parameter for predicting the precipitation of iron oxyhydroxide and the fate and transport of many metals. The formation of iron oxyhydroxide occurs by oxidation of iron (II) to iron (III) (usually by oxygen) followed by a precipitation or co-precipitation reaction.

### **Lead (Pb)**

Lead(+2) is the most common stable ionic aqueous species with hydroxyl, carbonate, sulfide, and sulfate anions acting as solubility controls. Under aerobic conditions,  $\text{PbSO}_4$ , and to a lesser extent  $\text{PbCO}_3$ , control lead solubility; whereas under anaerobic conditions,  $\text{PbS}$  concentrations mediate aqueous lead solubility. Lead may also exist in soluble organic complexes (i.e., humic and fulvic acids) in aqueous matrices. Lead-containing organo-metallic complexes may be other forms of

dissolved lead in aqueous matrices on site. Lead adsorbs principally to clays, hydrous iron and manganese oxides, mineral surfaces, and organic compounds. Lead adsorption is very pH-dependent, with low pH conditions favoring desorption. Lead is not appreciably bioaccumulated in aquatic organisms (BCF of 49 L/kg; EPA, 1986).

### **Manganese (Mn)**

Manganese occurs in the +2 and +4 oxidation states in aqueous systems. In oxidized waters, Mn(+4) is the stable form. Mn(+4) is insoluble and precipitates, along with Fe(+3), to form ferromanganous oxides and oxyhydroxides. In anaerobic waters, manganese is reduced to Mn(+2) which is soluble under continuing reducing conditions.

Studies of natural systems have shown that Mn(+4) is the first (i.e., the least soluble) metal to precipitate of the behaviorally analogous group of metals consisting of manganese, iron and arsenic. Similarly, the reduction of Mn(+4) to Mn(+2) and the accompanying re-dissolution occurs before the reduction of Fe(+3) or As(+5). Thus, as long as aerobic conditions persist in groundwater, transport of manganese in aqueous solution will be of minor significance. This is primarily the result of manganese readily forming insoluble oxides in aerobic waters, which often requires nucleation on a particle resulting in “manganese coatings.” The formation and continued growth of manganese coatings is an adsorption process that is important under aerobic conditions, but is readily reversed if conditions become anaerobic. Therefore, under anaerobic conditions, the transport of manganese in aqueous solution will be of greater significance. Information regarding the bioaccumulation of manganese in freshwater biota provides a BCF of less than 600 L/kg (ATSDR, 2014).

### **Mercury (Hg)**

Mercury may exist in the 0, +1, or +2 valence states in natural waters, depending on Eh-pH conditions. Above pH 5 and under moderately oxidizing conditions, dissolved elemental mercury is expected to be the predominant inorganic aqueous species. Mercury readily complexes with organic matter via biologically and non-biologically mediated processes. As a result, dissolved methyl mercury ion and undissociated dimethyl mercury may be present in aqueous matrices if mercury is present. Some studies have found mercury concentrations in surface waters vary with the biological cycle (i.e., vary seasonally with biological activity). Mercury is strongly absorbed to many inorganic surfaces and organic matter. Desorption may occur under low pH conditions. Mercury is substantially bioaccumulated in aquatic organisms (BCF of 5,500 L/kg; EPA, 1986), with a large percentage of the mercury being present as organo-mercurial compounds formed by microbes within the slim coat of the fish.

### **Nickel (Ni)**

Nickel almost always occurs as Ni(+2) in aquatic environments. Although conditions can favor the presence of dissolved nickel, in aqueous matrices, nickel may be primarily associated with the

particulate phases because of its strong adsorptive affinity. Nickel sorbs to hydrous iron, manganese oxides, clay minerals, and organic material. Nickel is not appreciably bioaccumulated in aquatic organisms (BCF of 47 L/kg; EPA, 1986).

### **Selenium (Se)**

Selenium is an essential nutrient, but can be toxic when only slightly above required levels. The geochemical behavior of selenium is similar to that of sulfur, and selenium occurs in both cationic (mostly +4) and anionic (-2) states. More rarely, selenium can occur in the native (0) state. However, this occurs only under anoxic conditions. Selenium does not bioaccumulate in aquatic organisms (BCF of 16 L/kg; EPA, 1986).

### **Silver (Ag)**

Silver (I) is the predominant species in natural waters, although it may also occur in the +2 and +3 valence states as a complex ion. Silver tends to be closely associated with iron-manganese oxide and oxyhydroxide precipitates under aerobic conditions. Strong adsorption to metal precipitates, clay minerals and organic matter limits the mobility of silver, especially at higher (>7.0) pH values. Silver also forms insoluble silver salts with many of the common inorganic ligands (e.g., chloride, carbonate). EPA, 1986 indicated a BCF of 3,080 L/kg, indicating a significant ability to bioaccumulate.

### **Thallium (Tl)**

Thallium occurs predominantly in the +2 valence state in natural systems, and is quite insoluble over the typically encountered Eh-pH range of most natural waters. Because of its low solubility and resultant low aqueous concentrations, thallium behavior is not well studied. There is some evidence that thallium is strongly adsorbed to metal oxides and clays and that it may be involved in the biological cycle. Thallium is substantially bioaccumulated in aquatic organisms (BCF of 10,000 L/kg; EPA, 1999).

### **Vanadium (V)**

Vanadium can occur in the +3, +4, and +5 valence states in the normal range of environmental conditions. In addition to the complexity introduced by the multiple oxidation states, the aqueous geochemistry of vanadium is further complicated by the bewildering variety of complex ions that vanadium may form. In simplified form, however, the chemical behavior of vanadium somewhat resembles that of chromium. In reducing environments, vanadium is insoluble, and its solubility increases as conditions become increasingly oxidizing. Vanadium is readily adsorbed by clays and organic matter. Adsorption by organic matter is probably more correctly a reductive, and therefore an immobilizing, reaction. Data regarding the bioaccumulation of vanadium in fish species are lacking.

**Zinc (Zn)**

In most natural waters, zinc occurs as the hydrated divalent (+2) cation. In organically polluted waters, complexing with organic compounds may be an important process. The solubility of zinc is strongly dependent on pH, with low pH favoring increased solubility. Zinc has a strong affinity for adsorption to hydrous metal oxides, clays, and organic matter. Adsorption of zinc is strongly favored at higher (>7) pH values. Zinc can be substantially bioaccumulated in aquatic organisms (BCF of 78,000 L/kg; EPA, 2014).